

Thermodynamic and Kinetic Processes Involved
in the Growth of Epitaxial GaN Thin Films

N. Newman, J. Ross and M. Rubin,

Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720

Our experimental results using reactive magnetron sputtering, combined with earlier literature, are used to understand the thermodynamic and kinetic processes involved in GaN film growth and the limiting factors involved in the incorporation of nitrogen during the growth process. We show that GaN films fabricated with low pressure growth techniques (< 0.1 Torr) such as sputtering and molecular beam epitaxy (MBE) are formed under meta-stable conditions with a non equilibrium kinetically limited reaction. For these methods, the growth process is controlled by a competition between the forward reaction which depends on the arrival of activated nitrogen species at the growing surface and the reverse reaction whose rate is limited by the unusually large kinetic barrier of decomposition of GaN. In practice, the thermally activated rate of decomposition sets an upper bound to the growth temperature.

Advances in producing high quality GaN in either bulk crystals or thin film form has progressed at a relatively slow rate compared to the other III-V systems. To date, the main obstacle in fabricating high quality GaN crystals for electronic applications has been control over the background and dopant concentrations during crystal growth and subsequent processing. All studies before 1987 reported the fabrication of material which typically contained a large free electron concentration (undoped material as low as 1.4×10^{17} [1], typically $10^{19} - 10^{20} \text{ cm}^{-3}$ [2-5]). The very high n-type conductivity was hypothesized to be due to a large concentration of nitrogen vacancies.[2] Within the last few years, undoped material with a reduced concentration has been produced using Metal Organic Chemical Vapor Deposition (MOCVD) ($4 \times 10^{16} \text{ cm}^{-3}$ [6], $<10^{16} \text{ cm}^{-3}$ [7]) and plasma/ion-assisted Molecular Beam Epitaxy (MBE) ($8 \times 10^{13} \text{ cm}^{-3}$ [8], $<10^{17} \text{ cm}^{-3}$ [9]). It is not apparent if this recent progress can be attributed to improvements in stoichiometry. In this letter, we report the production of GaN epitaxial films with very low free electron concentrations ($8.4 \times 10^{14} \text{ cm}^{-3}$) using reactive magnetron sputtering. This data, when combined with earlier literature, is used to understand the thermodynamic and kinetic processes involved in film growth and the factors that limit nitrogen incorporation during the growth process.

In order to produce GaN, it has been experimentally realized that high temperatures (~ 700 - 1400 C), activated nitrogen species, and/or high nitrogen pressures are necessary to overcome the large kinetic barriers of formation. The significant barriers for reaction are due to the high dissociation energy of the triple bond of the N_2 molecule (225.9 kCal/mole). [10] The GaN bond is also surprisingly strong when compared to other semiconductors; the dissociation energy of GaN is 206 kCal/mole compared to 109.8 kCal/mole for GaAs and 108.9 kCal/mole for Si.[10] The unusually strong bonding encountered for both N_2 and GaN makes the GaN thin-film growth process distinctly different from processes conventionally used for other thin film systems.

The high equilibrium pressure of N_2 at the elevated growth temperatures and the significant kinetic barriers to the epitaxial growth process greatly limit the range of conditions of high quality GaN thin film growth. Using bulk thermodynamic data from the literature,[1,5,11-15] and earlier

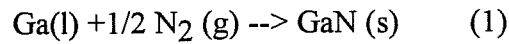
measurements of kinetic activation barriers for this system,[16] we show that our films are formed under meta-stable conditions using a non equilibrium kinetically-limited process. The forward reaction depends on the arrival of activated nitrogen species at the growing surface and the reverse reaction is rate limited by the unusually large kinetic barrier of decomposition of GaN.

The GaN films were deposited by reactive magnetron sputtering[17] using a 5 cm modular source produced by U.S. Inc. The target consisted of metallic Ga (99.999999%) held in a stainless steel cup. 110 W of rf power was typically applied to the sputter gun during film growth. R-plane (11 $\bar{2}$ 0) sapphire substrates were held in thermal contact with an electrically isolated heater. The target to substrate distance was 6.5 cm. The target was presputtered for 1 h in 10 mT of Ar and then in 10 mT of a 7:3 N₂:Ar mixture to create a nitrated surface on the target. Film properties were examined over a large range of substrate temperature (200-700 C), N₂ partial pressure (1.5-25 mTorr), N₂ flow rates (10-285 sccm) and N₂:Ar gas ratios (0.1-1.0). After deposition the substrates were cooled to below 200 C in 100 mT of N₂. Films were characterized by X-ray diffraction (Cu-K α radiation), Rutherford back scattering (RBS), 4-point probe, and Hall measurements. The data presented here includes the optimization and analysis of the electrical and structural properties of films produced over a wide range of growth conditions. The reader is referred to our early work[17] which includes a complete experimental description and photoluminescence optical characterization.

The substrate temperature affects the degree of crystallinity, composition, growth rate and resistivity, as shown in figure 1. At this N₂ partial pressure, (7 mTorr, 7:3 N₂:Ar, 70 sccm N₂ flow rate), a growth temperature of 650 C optimizes the crystallinity and nitrogen incorporation. The Full-Width-at-Half-Maximum (FWHM) of the (11 $\bar{2}$ 0) Θ -2 Θ X-ray diffraction peak for the 650 C sample is 25 minutes. For films within the epitaxial range (620-670 C), Hall carrier concentrations followed the resistivity data and varied from 5×10^{16} - 1×10^{19} cm⁻³. By further optimizing the N₂ partial pressure (8 mT), N₂ flow rate (238 sccm), N₂:Ar ratio (8:2), and substrate temperature of 650 C, stoichiometric films (N:Ga of 0.98 \pm 3%) with room temperature free electron

concentration as low as $8.4 \times 10^{14} \text{ cm}^{-3}$ with a Hall mobility of $330 \text{ cm}^2/(\text{V}\cdot\text{sec})$ were obtained. The value for the free electron concentration is comparable to $8 \times 10^{13} \text{ cm}^{-3}$, the lowest value reported for undoped material to date.[8]

Figure 2 shows the range of deposition conditions which were used in our study to produce GaN films, as well as the phase stability conditions of GaN for the following reactions.[1,5,11-15]



For comparison, typical deposition conditions for other GaN thin film growth techniques are also shown.[2,6-9,18-24]

The fact that high quality films can be grown in the unstable region of the phase diagram using reactive sputtering, ECR (electron cyclotron resonance) assisted-MOCVD[22], and plasma/ion-assisted MBE[8,9,19,20,22-24] is shown in Fig. 2. Only chemical vapor deposition (CVD) with the reactant NH_3 [1,3,6,18,21,25] utilizes growth conditions in the stable region of the GaN phase diagram. The very high gas pressures which are compatible with the MOCVD technique facilitates the use of high temperatures ($\sim 1000 \text{ C}$) while still in the stable phase region. These high temperatures are instrumental in overcoming the kinetic barriers of epitaxial growth. Recently, Choi et.al. and Khan et. al. have shown that successful MOCVD growth in the stable region of the phase diagram can also be achieved at lower temperatures (350-500 C) using plasma enhancement [26] or switched atomic layer epitaxy [7] to overcome kinetic barriers.

In contrast to CVD, other successful GaN thin-film growth techniques supplement the growth process with the introduction of activated nitrogen species using a plasma discharge[17], electron cyclotron resonance (ECR) plasma source,[9,19,20,22-24] or an ion gun[8]. This combined with the observation that successful growth occurs at significantly lower temperatures than for conventional CVD indicates that the activated species (e.g. N_2^+ , excited N_2 and/or atomic nitrogen)[27] are important in reducing both the free energy of reaction and overcoming the kinetic

barriers of the growth process.[28] The details of this type of growth process are difficult to access because of the poor quantitative understanding of the energy loss involved in the adsorption and diffusion process of the activated species on the growing epitaxial surface. In the following discussion, we try to elucidate the important rate controlling steps which are involved.

As seen in Figure 1a, substrate temperatures over 630 C are needed to obtain crystalline films for reactive sputter deposition. Fig. 1b and 1c also show that the net quantity of N and Ga incorporated into the film increases up to ~670 C. Even with the use of highly energetic nitrogen species, our data indicates that thermal energy on the growing surface is important for the uptake of both N and Ga under these conditions.

Temperatures above 680 C result in a loss of epitaxy, a drop in the growth rate, and a decreased N/Ga concentration ratio in the films. A number of possible mechanisms for the degradation in film properties would be consistent with this observation including a reduction in the sticking coefficient of the impinging Ga or N species, a re-evaporation of the diffusing species on the surface prior to incorporation into the GaN lattice, or the thermal decomposition of GaN.

Although there is little data on the kinetic parameters for reactive growth processes, we show that the measured rate of thermal decomposition is a fundamental limitation encountered when growing high quality GaN thin films. In contrast to thermodynamic predictions, GaN undergoes essentially congruent thermal decomposition in vacuum due to the unusually large kinetic barrier of GaN decomposition.[16] The decomposition reaction results in a vapor of Ga atoms and N₂ molecules with an average kinetic energy consistent with the measured GaN surface temperature.[30]

Figure 3 shows the comparison between the N₂⁺ arrival rate for GaN growth conditions in the ion-assisted MBE study of Powell et. al[8] and the rate of decomposition of GaN in vacuum, as measured by Munir and Searcy.[16] Note that high quality films were produced when the rate of arrival of the activated species was larger than the rate of sublimation. Because the mean free path at the 0.2 mT deposition pressures is ~40 cm, the extent of re-deposition is relatively small and the

rate of decomposition in vacuum as measured by Munir and Searcy is a reasonable estimate for our purposes. In practice, the kinetic barrier of decomposition determines an upper bound to the growth temperature in low pressure growth processes such as MBE since growth rates are typically on the order of several microns/hour.

In Fig. 3 we also compare the rate of deposition which was used in our study with the rate of decomposition. At 700 C, we observe a loss of epitaxy, a drop in the growth rate and a decreased N/Ga ratio. Under these conditions, the rate of GaN decomposition in vacuum as measured by Munir and Searcy is within a factor of ~ 100 of the growth rate. The large decrease in the growth rate between 680 and 700 C can not be explained by the process of GaN thermal decomposition alone. The impinging flux of energetic ions, electrons, atoms and/or molecules at the substrate surface could increase the rate of decomposition.[30] Non-stoichiometric surfaces may also affect the rate of decomposition through catalysis [31] and/or the law of mass action[32]. For the samples prepared at the highest temperature (700 C), we found a N:Ga ratio of ~ 0.7 . Schoonmaker et. al. reported that the GaN decomposition reaction can be significantly enhanced from catalysis by the presence of metallic Ga.[31] Although the specific mechanism for the loss in crystallinity at these elevated growth temperatures is not clear at this time, the rapid rate of re-evaporation (or re-sputtering) of the diffusing species prior to incorporation in the GaN lattice and the on going thermal decomposition are believed to inhibit epitaxy.

By comparing the growth rate data for different sputtering powers in our experiments, additional evidence for a significant rate of sublimation is found. Under similar conditions (650 C, 7 mT N₂, 3 mT Ar), a change from 110 W to 50 W of power to the Ga sputtering target results in a decrease in the N:Ga ratio from 92% to 66% and a disproportionate decrease in the growth rate from 2.4 Å/sec to 0.34 Å/sec.

It is unusual that the kinetic barrier of decomposition is of the same order as the heat of reaction, as is found for GaN. To illustrate the more common situation, we take as an example the fabrication of thin films of the high temperature superconductor oxide, YBa₂Cu₃O_{7- δ} . Successful

growth occurs only for growth conditions which fall in the stable region of the phase diagram.[33] Activated species are used to overcome kinetic barriers so that films can be grown at lower temperatures and pressures in the stable phase region. The rapid rate of decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prevents the growth of high quality material from occurring under meta-stable conditions as can be done with GaN.

In summary, high quality epitaxial GaN (11 $\bar{2}$ 0) layers have been grown on R-plane (01 $\bar{1}$ 2) sapphire with free carrier concentrations as low as $8 \times 10^{14}/\text{cm}^{-3}$ with Hall mobility's of $330 \text{ cm}^2/(\text{V sec})$. We have shown that GaN films fabricated with reactive magnetron sputtering, plasma/ion-assisted MBE, and ECR-assisted MOCVD are formed under meta-stable conditions. Although it is not clear if growing GaN films under meta-stable conditions is superior for thin film deposition, we observe that the lowest free electron concentrations measured in undoped GaN material have been obtained in our reactive sputtering study and in the ion assisted MBE study of Powell[8]. For these methods, we find that the growth process is controlled by a competition between the forward reaction which critically depends on the arrival of activated nitrogen species at the growing surface and the reverse reaction whose rate limiting step is the unusually large kinetic barrier of decomposition of GaN. When these processes are taken into account, very good quantitative agreement is found between the expected conditions of growth and the thermodynamic and kinetic data.

Acknowledgments

This work was supported by the U.S. Department of Energy under contract #DE-AC03-76SF00098 and the National Science Foundation under contract #1-442427-21482. The authors would like to thank K. Gustaffson and N. Cheung for helpful discussions.

References.

1. M. Ilegems and H. C. Montgomery, *J. Phys. Chem. Solids* 34, 885 (1973).
2. H. P. Maruska and J. J. Tietjen, *Appl. Phys. Lett.* 15, 327 (1969).
3. Masatoshi Sano and Masaharu Aoki, *Jap. J. Appl. Phys.* 15, 1943 (1976).
4. R. A. Logan and C. D. Thurmond, *J. Electrochem. Soc.* 119, 1727 (1972).
5. K. Gillessen, K. -H. Schuller and B. Struck, *Mat. Res. Bull.* 12, 955 (1977).
6. Shuji, Nakamura, *Jap. J. Appl. Phys.* 30, L1705 (1991).
7. M. Asif Khan, R. A. Skogman, J. M. Van Hove, D. T. Olson, and J. N. Kuznia, *Appl. Phys. Lett.* 60, 1366 (1992); M. Asif Khan, J. N. Kuznia, D. T. Olson, J. M. Van Hove, M. Blasingame, and L. F. Reitz, *Appl. Phys. Lett.* 60, 2917 (1992)
8. R. C. Powell, G. A. Tomasch, Y. -W. Kim, J. A. Thornton and J. E. Greene, *Mat. Res. Soc. Symp. Proc.* 162, 525 (1990).
9. T. Lei, T. D. Moustakas, R.J. Graham, Y. He and S. J. Berkowitz, *J. Appl. Phys.* 71, 4933 (1992).
10. *Handbook of Chemistry and Physics*, Ed. Robert C. Weast, David C. Lide, Melvin J. Astle, William H. Beyer, CRC Press, Boca Raton, Florida, p. D50-D53, 1990.
11. J. B. Mac Chesney, P. M. Bridenbaugh, and P. B. O' Connor, *Mat. Res. Bull.* 5, 783 (1970).
12. R. Juza and H. Hahn, *Z. Anorg. Z. Chem.* 244, 111 (1940); R. Juza and H. Hahn, *Z. Anorg. Z. Chem.* 244, 133 (1940).
13. M. R. Lorenz and B. B. Binkowski, *J. Electrochemical Society* 109, 24 (1962).
14. J. Karpinski, J. Jun, and S. Porowski, *Journal of Crystal Growth* 66, 1 (1984).
15. C. D. Thurmond and R. A. Logan, *Solid State Science and Technology* 119, 622 (1972).
16. Zuhair A. Munir, Alan W. Searcy, *Journal of Chemical Physics* 42, 4223 (1965).

17. J. Ross and M. Rubin, *Materials Letters* 12, 215 (1991).
18. M. Asif Khan, J. N. Kuznia, J. M. Van Hove, D. T. Olson, S. Krishnankutty and R. M. Kolbas, *Appl. Phys. Lett.* 58, 526 (1991).
19. M. J. Paisley, Z. Sitar, J. B. Posthill and R. F. Davis, *J. Vac. Sci. Technol.* A7, 701 (1989).
20. Z. Sitar, M. J. Paisley, B. Yan, J. Ruan, W. J. Choyke and R. F. Davis, *J. Vac. Sci. Technol.* B8, 316 (1990).
21. Toru Sasaki and Sakae Zembutsu, *J. Appl. Phys.* 61, 2533 (1987).
22. Hirotsguo Sato, Toru Sasaki, Takashi Matsuoka and Akinori Katsui, *Jap. J. Appl. Phys.* 29, 1654 (1990).
23. S. Strite, J. Ruan, Z. Li, A. Salvador, H. Chen, David J. Smith, W. J. Choyke, and H. Morkoc, *J. Vac. Sci. Technol.* B9, 1924 (1991).
24. G. Martin, S. Strite, J. Thornton and H. Markoc, *Appl. Phys. Lett.* 58, 2375 (1991).
25. B. Monemar, *Phys. Rev.* B10, 676 (1974).
26. S. W. Choi, K. J. Bachmann and G. Lucovsky, *Mat. Res. Soc. Symp.* 204, 195 (1991).
27. The release of the Ga heat of condensation at the growing surface may also aid in driving the forward reaction. This contribution is expected to be small because the energy is significantly less and the rate of thermalization is expected to be greater than those of the activated nitrogen species.
28. A recent study using MBE [R. C. Powell, N. -E. Lee and J. E. Greene, *Appl. Phys. Lett.* 60, 2505 (1992)] reports growth of GaN with a non-activated NH_3 species supplied locally by a substrate doser. Since the determination of the reported flux ($10^{17}/\text{cm}^3$) didn't take into account the directional flow and concentration gradient, the effective pressure of the substrate is difficult to determine and could be orders of magnitude higher than the background chamber pressure (3×10^{-4} Torr). Therefore, the NH_3 flux may correspond to a value in the stable regime of the phase diagram. If more careful considerations show that it falls under the critical stability line, this would

indicate that the heat of condensation of the Ga vapor can drive the forward reaction under these conditions.

29. Raymond W. Mar and Alan W. Searcy, J. Chem. Phys. 49, 182 (1968).

30. H. F. Winters and E. Kay, J. Appl. Phys. 38, 3928 (1967).

31. Richard C. Schoonmaker, Albert Buhl and James Lemley, The Journal of Phys. Chem. 69, 3455 (1965).

32. Gabor A. Somorjai, Science 162, 755 (1968).

33. R. H. Hammond and R. Bormann, Physica C 162-4, 703 (1989).

Figure Captions.

Fig. 1.

(a) The degree of crystallinity as judged by the intensity of the X-ray Bragg reflection for 2 μ m thick films; (b) the N/Ga concentration ratio as measured by Rutherford back scattering; (c) the growth rate and (d) resistivity of GaN films as a function of the substrate temperature for reactive sputtering in 70% N₂ and 10 mTorr total pressure.

Fig. 2.

Typical pressure and substrate temperatures which are used for the successful production of GaN using N₂ or NH₃ reactants. Also shown are lower (\uparrow) and upper (\downarrow) bounds of the critical stability line for phase equilibrium for reactions (1) and (2). The lower(upper) bound points indicate the conditions in which GaN is experimentally found to decompose (form). The points A,B,C,D and E in (a) correspond to references 11,14,12,13 and 5 respectively. The points in (b) are from the work and summary of Lorenz and Binkowski.[13] The theoretical critical stability lines as calculated by Thurmond et. al. [15] are also included.

Fig. 3.

A comparison of the flux of nitrogen incorporated into the films in our study, the flux of N₂⁺ used for successful GaN growth in the ion assisted MBE study of Powell et. al. [8] and the experimentally determined flux from the measurements of the sublimation rate of GaN in vacuum from Munir and Searcy[16] resulting from the kinetic barrier of decomposition.

Fig 1.

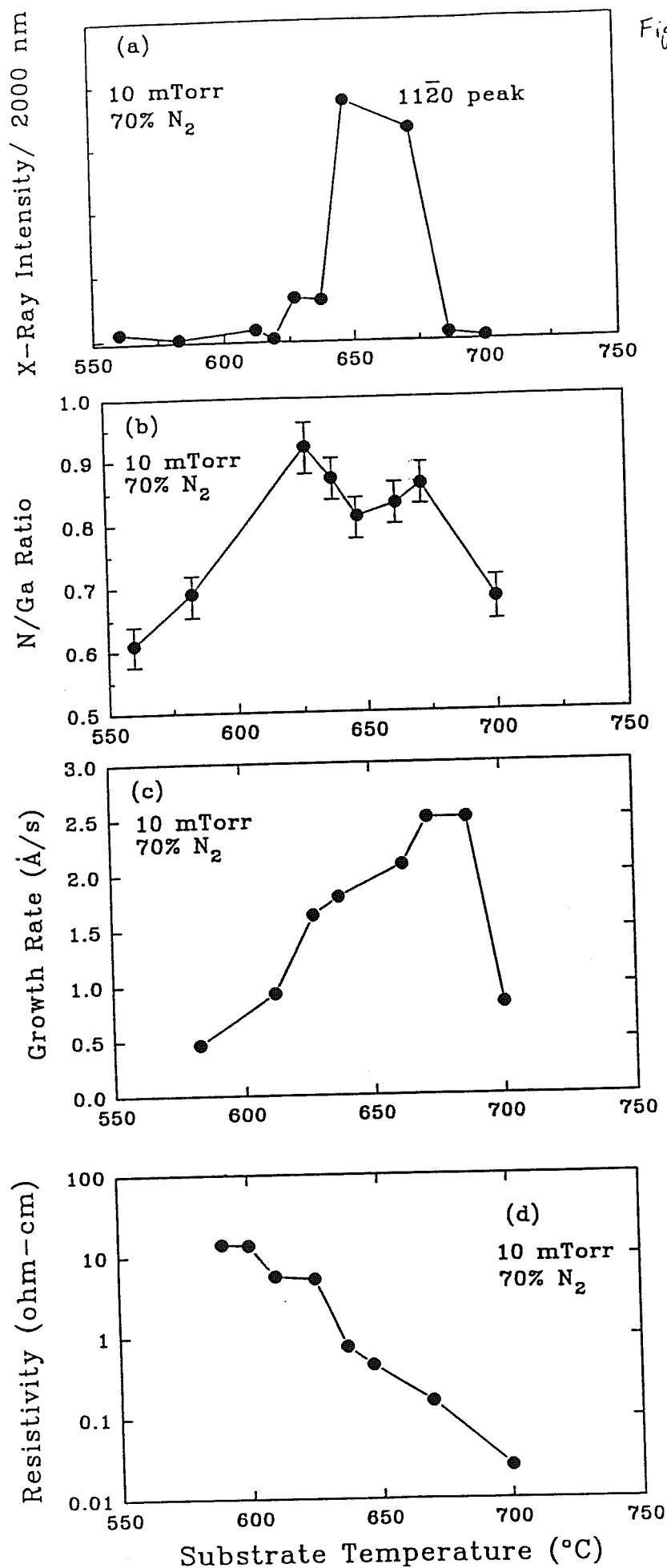


Figure 2a ³

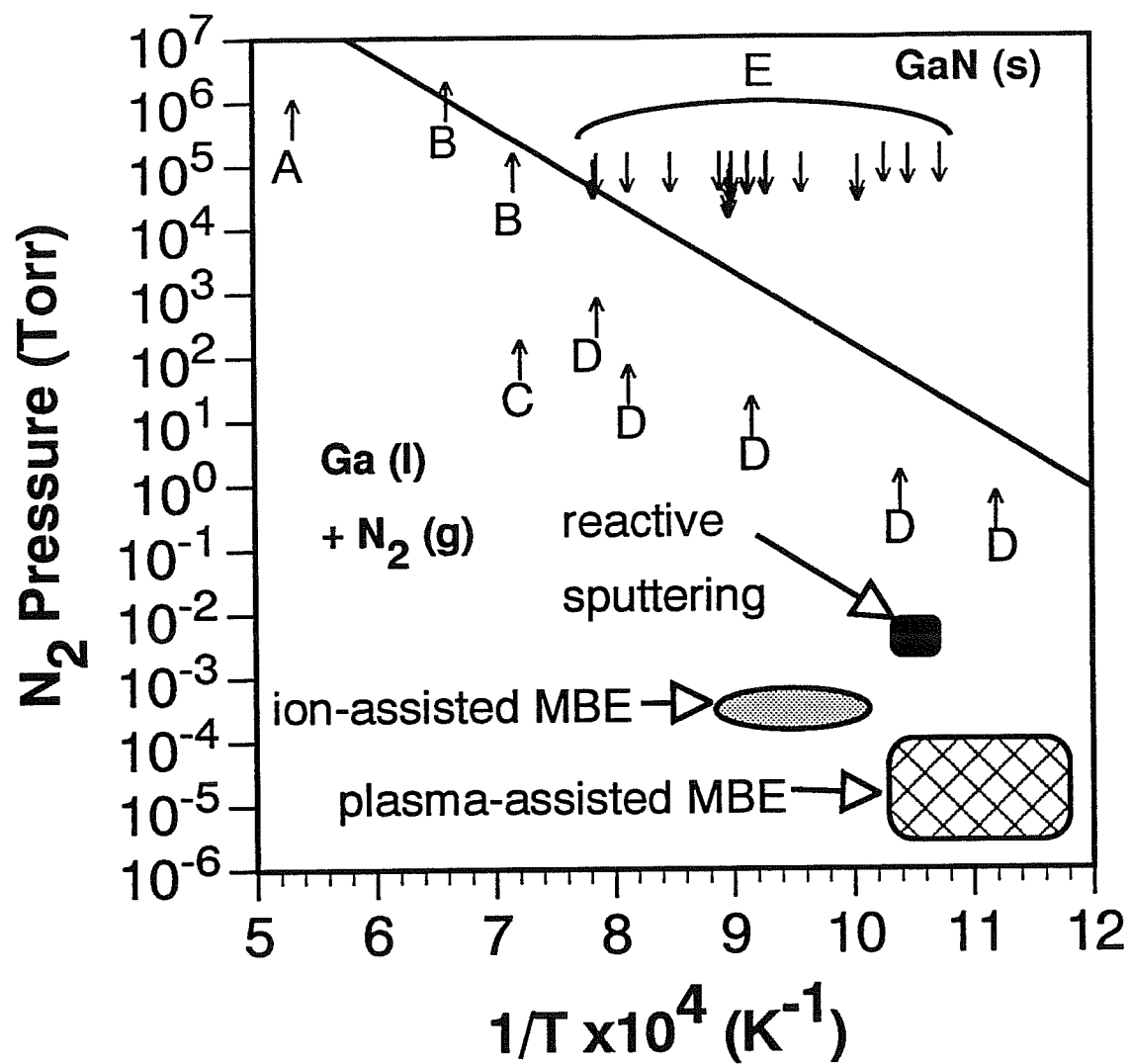


Figure 2b

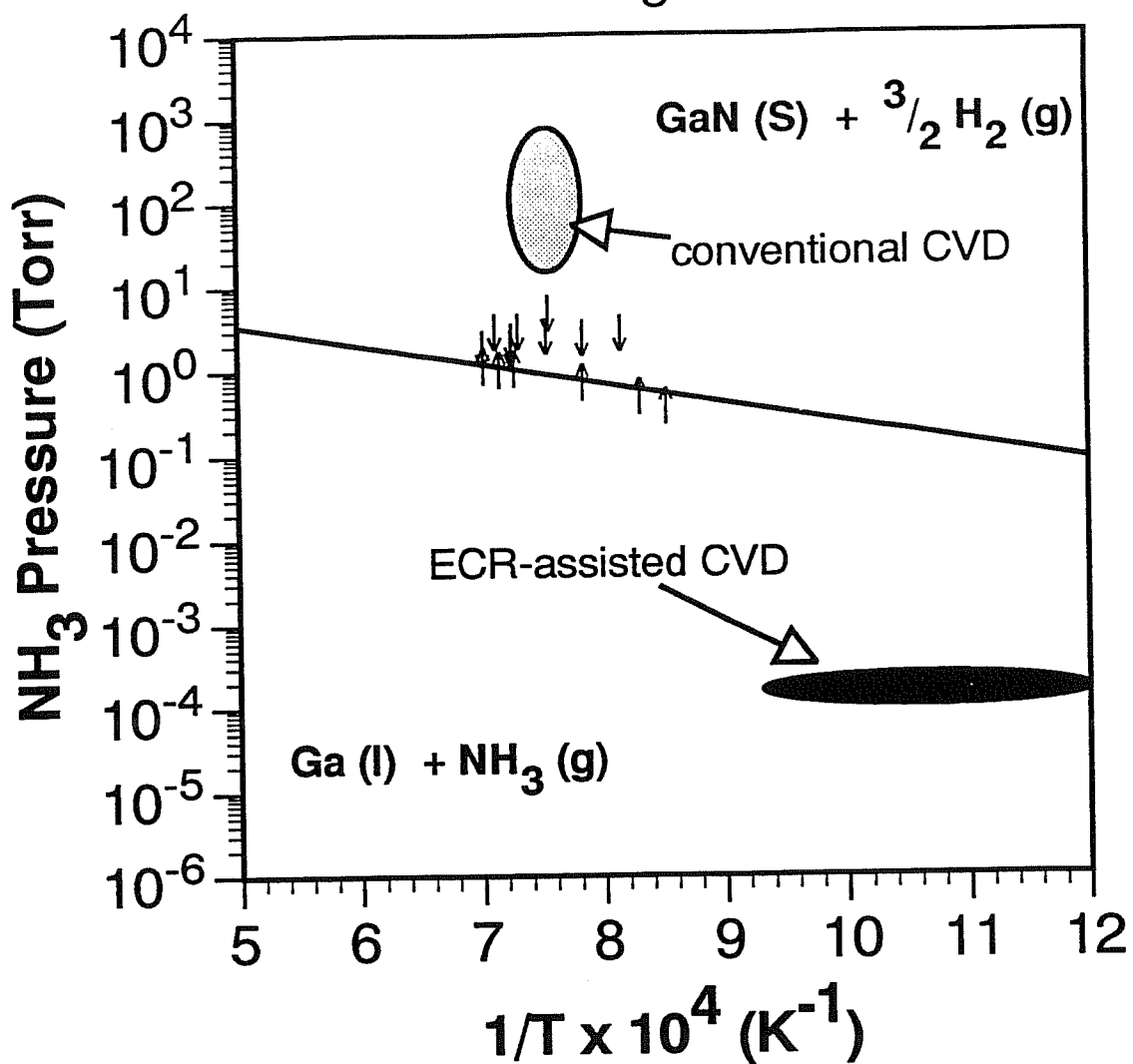


Fig. 3

